JP Patent Application: Sho 63-229379(13.9.1988)
JP Patent Kokai : Hei 2-75618(15.3.1990)
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- Specification -

1. Title of Invention

Resin composition for use in optical modelling

2. Claim

(1) A resin composition for use in optical modelling characterized by comprising, as essential ingredients, (a) an energy beam-curable, cation-polymerizable organic substance, (b) an energy beam-sensitive, cationic polymerization initiator, (c) an energy beam-curable, radical-polymerizable organic substance, (d) an energy beam-sensitive radical polymerization initiator and (e) a hydroxyl group-containing polyester.

(2) A resin composition for use in optical modelling according to Claim 1, characterized in that said energy beam-curable, cation-polymerizable organic substance (a) contains an alicyclic epoxy resin having at least two epoxy groups in one molecule in an amount of no less than 40% by weight and

said energy beam-curable, radical-polymerizable organic substance (c) contains a compound having at least three unsaturated double bonds in one molecule in an amount of no less than 50% by weight.

3. Detailed Description of the Invention

[Industrial Field of the Invention]

The present invention relates to an active energy beam-curable resin composition for use in optical modelling.

[Prior Art and Problem to be Solved by the Invention]

The model according to the shape of which a casting mold is formed, the model for the follow-up control of cutting fabrication, and the model electrode for use in the discharge-engraving fabrication have generally been prepared so far either manually or by NC cutting method using an NC milling machine. However, the manual fabrication is disadvantageous in that it demands much labor and skillfulness, and the NC cutting fabrication is disadvantageous in that it requires a complicated program for altering the shape of cutting edge or for coping with attrition of cutting edge and sometimes requires a finishing process. Thus, it is desired in the recent time to develop a new technique capable of solving the above-mentioned problems of prior art and giving models for casting mold, models for follow-up control, complicated models for discharge-engraving fabrication, or a variety of modelled products by the method of optical modelling.

The resin for use in the optical modelling must fulfil various requirements such as superiority in energy beam-curing sensitivity, high resolution in energy beam curing, high ultraviolet transmittance after cure, low viscosity, good gamma characteristics, small volume shrinkage of cured product, excellent mechanical properties of cured product, good self-adhesiveness, good curing property in oxygen atmosphere, etc.

On the other hand, Japanese Patent Kokai Sho 62-235318 discloses a technique characterized by simultaneously photo-curing an epoxy compound having at least two epoxy groups in one molecule and a vinyl compound having at least two vinyl groups in one molecule by the use of a triaryl sulfonium salt catalyst. However, since the process of the above-mentioned technique does not aim at obtaining a resin for use in optical modelling, the resin obtained by said technique is not suitable for use in an optical modelling system.

[Means for Solution of the Problem]

The present invention is based on extensive studies on a photosensitive resin fulfilling the above-mentioned conditions required of a resin for use in optical modelling.

The object of the present invention is to provide a resin composition most suitable for use in an optical modelling system using active energy beams.

The resin composition of the present invention for use in optical modelling is characterized by comprising, as essential ingredients, (a) an energy beam-curable, cation polymerizable organic substance, (b) an energy beam-sensitive, cationic polymerization initiator, (c) an energy beam-curable, radical-polymerizable organic substance, (d) an energy beam-sensitive radical polymerization initiator and (e) a hydroxyl group-containing polyester.

The energy beam-curable cation-polymerizable organic substance (a) used as a constituent of the present invention is a cation-polymerizable compound which takes part in a polymer-forming or crosslinking reaction when irradiated with an energy beam in the presence of an energy beam-sensitive cationic polymerization initiator (b). Examples of such compound include epoxy compounds, cyclic ether compounds, cyclic lactone compounds, cyclic acetal compounds, cyclic thioether compounds, spiro-orthoester compounds, vinyl compounds and the like and mixtures of two or more of these compounds. Of these cation-polymerizable compounds, those having at least two epoxy groups in one molecule are particularly preferable, and such compounds include hitherto known aromatic epoxy resins, alicyclic epoxy resins and aliphatic epoxy resins.

As the aromatic epoxy resin, preferable are polyglycidyl ethers of polyhydric phenols having at least one aromatic nucleus or alkylene oxide adducts thereof. Examples include glycidyl ethers produced by reacting epichlorohydrin with Bisphenol A, Bisphenol F, or alkylene oxide adduct thereof, and epoxy novolac resin.

As the alicyclic epoxy resin, preferable are polyglycidyl ethers of polyhydric alcohols having at least one alicyclic group, and cyclohexene oxide- or cyclopentene oxide-containing compounds obtained by epoxidizing a cyclohexene ring- or cyclopentene ring-containing compound with an appropriate oxidant such as hydrogen peroxide, peracid or the like. Typical examples of such alicyclic epoxy resin include hydrogenated Bisphenol A diglycidyl ether, 3,4-epoxycyclohexylmethyl 3,4-epoxycyclohexanecarboxylate, 2-(3,4-epoxycyclohexyl-5,5-spiro-3,4-epoxy)-cyclohexane-meta-dioxane, bis(3,4-epoxycyclohexylmethyl) adipate, vinylcyclohexene dioxide, 4-vinylepoxycyclohexane, bis(3,4-epoxy-6-methylcyclohexylmethyl) adipate, 3,4-epoxy-6-methylcyclohexyl 3,4-epoxy-6-methylcyclohexanecarboxylate, methylenebis(3,4-epoxycyclohexane), dicyclopentadiene diepoxide, ethylene glycol di(3,4-epoxycyclohexylmethyl) ether, ethylenebis(3,4-epoxycyclohexanecarboxylate), dioctyl epoxyhexahydrophthalate, di-2-ethylhexyl epoxyhexahydrophthalate, and the like.

As the aliphatic epoxy resin, preferable are polyglycidyl ethers of aliphatic polyhydric alcohols and alkylene oxide adducts thereof, polyglycidyl esters of aliphatic long-chained polybasic acids, and homopolymers and copolymers of glycidyl acrylate and glycidyl methacrylate. Typical examples of the aliphatic epoxy resin include 1,4-butanediol diglycidyl ether, 1,6-hexanediol diglycidyl ether, glycerin triglycidyl ether, trimethylolpropane triglycidyl ether, sorbitol tetraglycidyl ether, dipentaerythritol hexaglycidyl ether, polyethyleneglycol diglycidyl ether, polypropyleneglycol diglycidyl ether, polyglycidyl ethers of polyether-polyols obtained by adding at lest one kind of alkylene oxide to an aliphatic polyhydric alcohol such as ethylene glycol, propylene glycol, glycerin or the like, and diglycidyl esters of aliphatic long-chained dibasic acids. Further, monoglycidyl ethers of aliphatic higher alcohols, monoglycidyl ethers of phenol, cresol, butylphenol or polyether-alcohols obtained by adding an alkylene oxide thereto, glycidyl esters of higher fatty acids, epoxidized soybean oil, butyl epoxystearate, octyl epoxystearate, epoxidized linseed oil, epoxidized polybutadiene and the like are also included.

Examples of cation-polymerizable organic substances other than the epoxy compounds include the following:

oxetane compounds such as trimethylene oxide, 3,3-dimethyloxetane, 3,3-dichloromethyloxetane and the like; oxorane compounds such as tetrahydrofuran, 2,3-dimethyltetrahydrofuran and the like; cyclic acetal compounds such as trioxane, 1,3-dioxorane, 1,3,6-trioxane-cyclooctane and the like; cyclic lactone compounds such as β-propiolactone, ε-caprolactone and the like; thiirane compounds such as ethylene sulfide, thioepichlorohydrin and the like; thiethane compounds such as 1,3-propyne sulfide, 3,3-dimethylthiethane and the like; vinyl ether compounds such as ethylene glycol divinyl ether, alkyl vinyl ether, 3,4-dihydropyran-2-methyl (3,4-dihydropyran-2-carboxylate), triethylene glycol divinyl ether and the like; spiro-ortho-ester compounds obtained by reacting an epoxy compound with a lactone; ethylenically unsaturated compounds such as vinylcyclohexane, isobutylene, polybutadiene and the like; and derivatives of the abovementioned compounds. These cation-polymerizable compounds can be put to use either singly or after mixing two or more compounds so as to exhibit a desired property.

Of these cation-polymerizable organic substances, particularly preferable are alicyclic epoxy resins having at least two epoxy groups in one molecule. Such epoxy resins are excellent in various properties such as cation-polymerizability, lowness in viscosity, ultraviolet transmitting property, thick film curability, volume shrinkage, resolution, etc.

The energy beam-sensitive cationic polymerization initiator (b) used in the present invention is a compound capable of releasing a cationic polymerization-initiating substance when irradiated with an energy beam. Particularly preferable compounds of this type are onium type double salts releasing a Lewis acid upon irradiation. Typical examples of such compounds are those expressed by the following general formula:

$$[R^1_aR^2_bR^3_cR^4_dZ]^{+m}[MX_{n+m}]^{-m}$$

wherein the cation is an onium; Z is S, Se, Te, P, As, Sb, Bi, O, halogen such as I, Br or Cl, or N=N; R^1, R^2, R^3 and R^4 are identical or different organic groups; a, b, c and d are each an integer of 0-3, provided that a+b+c+d is equal to valency of Z; M is a metal or metalloid functioning as a central atom of the halogenide complex, selected from B, P, As, Sb, Fe, Sn, Bi, Al, Ca, In, Ti, Zn, Sc, V, Cr, Mn, Co and the like; X is halogen; m is net charge of halogenide complex ion; and n is number of atoms in the halogenide complex ion.

Examples of the anions expressed by general formula MX_{n+m} include tetrafluoroborate (BF_4^-), hexafluorophosphate (PF_6^-), hexafluoroantimonate (SbF_6^-), hexafluoroarsenate (AsF_6^-), hexachloroantimonate ($SbCl_6^-$), and the like.

Anions expressed by a general formula $MX_n(OH)^-$ can also be used in the invention. Some other anions are also usable in the invention, which are perchlorate ion (ClO_4^-), trifluoromethyl-sulfite ion ($CF_3SO_3^-$), fluorosulfonate ion (FSO_3^-), toluenesulfonate anion, trinitrobenzenesulfonate anion, and the like.

Of these onium salts, aromatic onium salts are particularly effectively usable as the cationic polymerization initiator. Among aromatic onium salts, preferred are the aromatic halonium salts mentioned in JP-A-50-151996 [this means Japanese Patent Kokai (Unexamined Publication) Sho 50-151996, hereinafter the same] and JP-A-50-158680; the Group VIA element-aromatic onium salts mentioned in JP-A-50-151997, JP-A-52-30899, JP-A-56-55420 and JP-A-55-125105; the Group VA element-aromatic onium salts mentioned in JP-A-50-158698; the oxosulfonium salts mentioned in JP-A-56-8428, JP-A-56-149402, JP-A-57-192429, etc.; the aromatic diazonium salts mentioned in Japanese Patent Kokoku (Examined Publication) Sho 49-17040; and the thiopyrylium salts mentioned in US Patent No. 4139655. Further, initiators of iron/allene complex type and aluminum complex/photodecomposable silicon compound type are also preferably usable.

The above-mentioned cationic polymerization initiators can be used in combination with a photosensitizer such as benzophenone, benzoin isopropyl ether, thioxanthone and the like.

The energy beam-curable radical-polymerizable organic substance (c) used in the invention is a radical-polymerizable compound which can form a polymer or a crosslinkage when irradiated with an energy beam in the presence of an energy beam-sensitive radical polymerization initiator (d). Examples of such a substance (c) include acrylate compounds, methacrylate compounds, allylurethane compounds, unsaturated polyester compounds, polythiol compounds and mixtures of two or more of these compounds. Of these radical-polymerizable compounds, preferable are those having at least one acryl group in one molecule. Examples of such preferable compounds include epoxyacrylates, urethane acrylates, polyester-acrylates, polyether-acrylates and alcohol acrylates.

As the epoxy-acrylate, preferable are the acrylates obtained by reacting acrylic acid with hitherto known aromatic epoxy resin, alicyclic epoxy resin, aliphatic epoxy resin or the like. Of these epoxy-acrylates, particularly preferable are aromatic epoxy resin acrylates obtained by reacting acrylic acid with a polyglycidyl ether of a polyhydric phenol having at least one aromatic nucleus or an alkylene oxide adduct thereof. As examples of such aromatic epoxy resin acrylate, an acrylate obtained by reacting acrylic acid with a glycidyl ether obtained by reacting epichloro-hydrin with Bisphenol A or an alkylene oxide adduct thereof, and an acrylate obtained by reacting acrylic acid with an epoxy novolac resin can be referred to.

As said urethane acrylate, preferable are an acrylate obtained by reacting a hydroxyl group-containing acrylic ester and an isocyanate with at least one hydroxyl group-containing polyester or hydroxyl group-containing polyether, and an acrylate obtained by reacting an isocyanate with a hydroxyl group-containing acrylic ester. As the hydroxyl group-containing polyester used herein, preferable are those obtained by esterifying at least one aliphatic polyhydric alcohol with at least one polybasic acid. As the aliphatic polyhydric alcohol, 1,3-butanediol, 1,4-butanediol, 1,6-hexanediol, diethylene glycol, triethylene glycol, neopentyl glycol, polyethylene glycol, polyethylene glycol, polypropylene glycol, trimethylolpropane, glycerin, pentaerythritol and dipentaerythritol can be used. As the polybasic acid, adipic acid, terephthalic acid, phthalic anhydride and trimellitic acid can be used. As the hydroxyl group-containing polyether, preferable are those obtained by adding at least one kind of alkylene oxide to an aliphatic polyhydric alcohol. As the aliphatic polyhydric alcohol, 1,3-butanediol, 1,4-butanediol, 1,6-hexanediol, diethylene glycol, triethylene glycol, neopentyl glycol, polyethylene glycol, polypropylene glycol, trimethylolpropane, glycerin, pentaerythritol and dipentaerythritol can be used, for example. As the alkylene oxide, ethylene oxide and propylene oxide can be used, for example. As the hydroxyl group-containing acrylic ester, preferable are those obtained by esterifying an aliphatic polyhydric alcohol with acrylic acid. As the aliphatic polyhydric alcohol, ethylene glycol, 1,3-butanediol, 1,4-butanediol, 1,6-hexanediol, diethylene glycol, triethylene glycol, neopentyl glycol, polyethylene glycol, polypropylene glycol, trimethylolpropane, glycerin, pentaerythritol and dipentaerythritol can be used, for example. Of such hydroxyl group-containing acrylic esters, particularly preferable are those obtained by esterifying an aliphatic dihydric alcohol with acrylic acid, of which examples include 2-hydroxyethyl acrylate. As said isocyanate, those having at least one isocyanato group in one molecule are preferable, and divalent isocyanate compounds such as tolylene diisocyanate, hexamethylene diisocyanate, isophorone diisocyanate and the like are particularly preferable.

As the polyester-acrylate, preferable are those obtained by reacting acrylic acid with a hydroxyl group-containing polyester. As the hydroxyl group-containing polyester used herein, preferable are those obtained by esterifying at least one aliphatic polyhydric alcohol with at least one monobasic acid, polybasic acid or phenol. As said aliphatic polyhydric alcohol, 1,3-butanediol, 1,4-butanediol, 1,6-hexanediol, diethylene glycol, triethylene glycol, neopentyl glycol, polyethylene glycol, polypropylene glycol, trimethylolpropane, glycerin, pentaerythritol and dipentaerythritol can be used, for example. As said monobasic acid, formic acid, acetic acid, butylcarboxylic acid and benzoic acid can be used, for example. As said polybasic acid, adipic acid, terephthalic acid, phthalic anhydride and trimellitic acid can be used, for example. As said phenol, phenol and p-nonylphenol can be used, for example.

As the polyether-acrylate, preferable are those obtained by reacting acrylic acid with a hydroxyl group-containing polyether. As said hydroxyl group-containing polyether used herein, preferable are those obtained by adding at least one kind of alkylene oxide to an aliphatic polyhydric alcohol. As said aliphatic polyhydric alcohol, 1,3-butanediol, 1,4-butanediol, 1,6-hexanediol, diethylene glycol, triethylene glycol, neopentyl glycol, polyethylene glycol, polypropylene glycol, trimethylolpropane, glycerin, pentaerythritol and dipentaerythritol can be used, for example. As said alkylene oxide, ethylene oxide and propylene oxide can be used, for example.

As the alcohol acrylate, preferable are those obtained by reacting acrylic acid with an aromatic alcohol or an aliphatic alcohol having at least one hydroxyl group in one molecule or an alkylene adduct thereof. Examples of such alcohol acrylate include 2-ethylhexyl acrylate, 2-hydroxyethyl acrylate, 2-hydroxypropyl acrylate, isoamyl acrylate, lauryl acrylate, stearyl acrylate, isooctyl acrylate, tetrahydrofurfuryl acrylate, isobornyl acrylate, benzyl acrylate, 1,3-butanediol diacrylate, 1,4-butanediol diacrylate, 1,6-hexanediol diacrylate, diethylene glycol diacrylate, triethylene glycol diacrylate, neopentyl glycol diacrylate, polyethylene glycol diacrylate, polypropylene glycol diacrylate, trimethylolpropane triacrylate, pentaerythritol triacrylate and dipentaerythritol hexaacrylate.

Of these acrylates, polyacrylates of polyhydric alcohols are particularly preferred.

In accordance with the desired properties, the above-mentioned radical-polymerizable organic substances may be used either singly or in combination of two or more.

Of the energy beam-curable radical-polymerizable organic substances (c) mentioned above, particularly preferable are those having at least three unsaturated double bonds in one molecule.

The energy beam-sensitive radical polymerization initiator (d) used in the present invention is a compound capable of releasing a radical polymerization-initiating substance when irradiated with an energy beam. Preferable examples of such initiator (d) are ketone type compounds such as acetophenone compounds, benzoin ether compounds, benzil compounds, benzophenone compounds, thioxanthone compounds and the like. As the acetophenone compound, diethoxyacetophenone, 2-hydroxymethyl-1-phenylpropan-1-one, 4'-isopropyl-2-hydroxy-2-methyl-propiophenone, 2-hydroxy-2-methyl-propiophenone, p-dimethylaminoacetophenone, p-tert-butyldichloroacetophenone, p-tert-butyltrichloroacetophenone and p-azidobenzalacetophenone can be used, for example. As the benzoin ether compound, benzoin, benzoin methyl ether, benzoin ethyl ether, benzoin isopropyl ether, benzoin n-butyl ether and benzoin isobutyl ether can be used, for example. As the benzil compound, benzil, benzil dimethyl ketal, benzil β-methoxyethyl acetal and 1-hydroxycyclohexyl phenyl ketone can be used, for example. As the benzophenone compound, benzophenone, methyl o-benzoylbenzoate, Michler's ketone, 4,4'-bisdiethylaminobenzophenone and 4,4'-dichlorobenzophenone can be used, for example. As the thioxanthone compound, thioxanthone, 2-methylthioxanthone, 2-ethylthioxanthone, 2-chlorothioxanthone and 2-isopropylthioxanthone can be used, for example.

In accordance with the desired properties, the above-mentioned energy beam-sensitive radical polymerization initiators (d) can be used either singly or in combination of two or more.

The hydroxyl group-containing polyester (e) used in the present invention includes the hydroxyl group-containing polyesters obtained by esterifying at least one aliphatic polyhydric alcohol with at least one monobasic acid, polybasic acid or phenol and the hydroxyl group-containing polyesters obtained through an esterification reaction between at least one lactone compound and at least one monobasic acid, polybasic acid or phenol. As said aliphatic polyhydric alcohol, 1,3-butanediol, 1,4-butanediol, 1,6-hexanediol, diethylene glycol, triethylene glycol, neopentyl glycol, polyethylene glycol, polypropylene glycol, trimethylolpropane, glycerin, pentaerythritol and dipentaerythritol can be used, for example. As said monobasic acid, formic acid, acetic acid, butylcarboxylic acid and benzoic acid can be used, for example. As said polybasic acid, adipic acid, terephthalic acid, phthalic anhydride and trimellitic acid can be used, for example. As said phenol, phenol and p-nonylphenol can be used, for example. As said lactone, β-propiolactone and ε-caprolactone can be used, for example.

The hydroxyl group-containing polyester (e) can be used either singly or in combination of two or more in accordance with the properties desired.

Next, compounding ratios between the energy beam-curable cation-polymerizable organic substance (a), the energy beam-sensitive cationic polymerization initiator (b), the energy beam-curable radical-polymerizable organic substance (c), the energy beam-sensitive radical polymerization initiator (d) and the hydroxyl group-containing polyester (e) will be mentioned in terms of parts by weight.

In the present invention, the compounding ratio between the energy beam-curable cation-polymerizable organic substance (a) and the energy beam-curable radical-polymerizable organic substance (c) is preferably 40-95 parts of (a) vs. 5-60 parts of (c), and further preferably 50-90 parts of

(a) vs. 10-50 parts of (c), provided that the sum of (a) and (c) is taken as 100 parts. When the compounding ratio between (a) and (c) is in such a range, the resin composition can exhibit particularly excellent properties as a resin composition for use in optical modelling.

In order to exhibit desired properties as a resin composition for optical modelling, the resin composition of the present invention may comprise a plurality of energy beam-curable cation-polymerizable organic substances (a) and a plurality of energy beam-curable radical-polymerizable organic substances (c).

The content of the energy beam-sensitive cationic polymerization initiator (b) may be in the range of 0.1-10 parts and preferably 0.5-6 parts, per 100 parts of the total energy beam-curable organic substances, namely 100 parts of the sum of the energy beam-curable cation-polymerizable organic substances (a) and the energy beam-curable radical-polymerizable organic substances (c). The content of the energy beam-sensitive radical polymerization initiator (d) may be in the range of 0.1-10 parts and preferably 0.2-5 parts, per 100 parts of the sum of energy beam-curable organic substances. In order to exhibit desired properties as a resin composition for use in optical modelling, the resin composition of the present invention may comprise a plurality of energy beam-sensitive cationic polymerization initiators (b) and a plurality of energy beam-sensitive radical polymerization initiators (d). In compounding these polymerization initiators with the energy beam-curable organic substances, the polymerization initiators may be used in the form of a solution in an appropriate solvent.

The content of the hydroxyl group-containing polyester (e) used in the present invention is preferably in the range of 5-40 parts and further preferably 10-30 parts, per 100 parts of the energy beam-curable cation-polymerizable organic substance (a) and the energy beam-curable radical-polymerizable organic substance (c). When the content of (e) is in such a range, the composition can exhibit particularly excellent properties as a resin composition for optical modelling.

In the composition of the present invention, a plurality of hydroxyl group-containing polyesters (e) may be compounded and used in order to exhibit the desired properties as a resin composition for optical modelling.

As above, in the composition of the invention, the hydroxyl group-containing polyester (e) is used in an amount of 5-40 parts by weight per 100 parts by weight of the sum of the energy beam-curable cation-polymerizable organic substance (a) and energy beam-curable radical-polymerizable organic substance (c), and thereby cure of the composition can be accelerated and excellent properties as a resin composition for optical modelling can be exhibited. Particularly when the content of hydroxyl group-containing polyester (e) is in the range of 10-30 parts per 100 parts of the sum of energy beam-curable cation-polymerizable organic substance (a) and energy beam-curable radical-polymerizable organic substance (c), a quite excellent resin composition for optical modelling can be obtained.

When the amount of the energy beam-curable cation-polymerizable organic substance (a) is larger than the amount prescribed by the above-mentioned compounding ratio, namely when the amount of the energy beam-curable radical-polymerizable organic substance (c) is smaller than the amount prescribed by the above-mentioned compounding ratio, the composition is not readily affected by the atmospheric oxygen at the time of curing reaction caused by active energy beam, and the volume shrinkage at the time of cure can be made smaller which reduces the tendency of forming cracks and strains in cured product, and further a resin composition of low viscosity can easily be obtained which can shorten the period of time necessary for modelling. In such a composition, however, the polymerization reaction readily propagates from the energy beam-irradiated part to the neighboring areas, due to which the resin composition is low in resolution and some period of time (a few seconds) is necessary from the time of the energy beam irradiation to the completion of polymerization. On the other hand, when the amount of the energy beam-curable cation-polymerizable organic substance (a) is smaller than the amount prescribed by the above-mentioned compounding ratio, namely when the amount of the energy beam-curable radical-polymerizable organic substance (c) is larger than the amount prescribed by the above-mentioned compounding ratio, the polymerization reaction does not readily propagate from the irradiated part to the neighboring areas, due to which the resolution is good and no significant period of time is necessary from the time of active energy beam irradiation to completion of polymerization. In such a composition, how ver, the energy beam-caused curing reaction or the polymerization reaction is apt to be retarded by the atmospheric oxygen, and the curing reaction is accompanied by a great volume shrinkage due to which strains and cracks are readily formed at the time of cure, and further the use of a low-viscosity type radical-polymerizable resin which must be used for the purpose of lowering the viscosity causes a remarkable irritation of the skin. The above-mentioned two types of resin composition are both unsuitable for use as a resin composition for optical modelling.

When the resin composition of the present invention for use in optical modelling is so prepared that the energy beam-curable cation-polymerizable organic substance (a) contains an alicyclic epoxy resin having at least two epoxy groups in one molecule in an amount of no less than 40% by weight and the energy beam-curable radical-polymerizable organic substance (c) contains a compound having at least three unsaturated double bonds in one molecule in an amount of no less than 50% by weight, there can be obtained a very excellent optical modelling system high in energy beam-reactivity, mechanical strength and resolution and having a volume shrink of 3% or less.

Into the resin composition of the present invention, a heat-sensitive cationic polymerization initiator, a colorant such as pigment and dye, various resin additives such as antifoaming agent, levelling agent, thickener, flame-retardant, antioxidant and the like, a filler such as silica, glass powder, ceramic powder, metal powder and the like, a modifying resin, etc. may be incorporated appropriately, so long as the effect of the present invention is not deteriorated by using them. As the heat-sensitive cationic polymerization initiator, the aliphatic onium salts mentioned in JP-A-57-49613 and JP-A-58-37004 can be used, for example.

Viscosity of the resin composition of the invention is preferably 2,000 cps or less and further preferably 1,000 cps or less at ordinary temperature. Too high a viscosity is undesirable because the period of time necessary for modelling becomes longer and the workability becomes worse when viscosity becomes higher.

From the viewpoint of dimensional accuracy, a resin composition for optical modelling is required to show a small volume shrink at the time of cure. The resin composition of the present invention should show a volume shrink at the time of cure of no greater than 5% and further preferably no greater than 3%.

The concrete procedure for practice of the present invention is as mentioned in JP-A-60-247515. Thus, a resin composition for optical modelling of the present invention is placed in a vessel, a light-conductive material is inserted into the resin composition, and an active energy beam necessary for cure of the composition is supplied from the light-conductive material while shifting the light-conductive material relatively to the vessel. Thus, a solid material having a desired shape can be formed. As the active energy beam used for curing the composition of the invention, ultraviolet ray, electron beam, X ray, radiations, and high-frequency wave can be referred to. Among these active energy beams, ultraviolet rays having a wavelength of from 1,800 to

5,000 angstroms are economically preferable, and as light source thereof, ultraviolet laser, mercury lamp, xenon lamp, sodium lamp, alkali metal lamp and the like can be used. Particularly preferable sources are laser sources which can enhance the energy level and thereby shorten the time period of modelling. Further, they can improve the accuracy of modelling owing to the good converging character. Point sources obtained by concentrating the ultraviolet rays emitted from various sources such as mercury lamp and the like are also usable effectively. In order to supply an active energy beam necessary for cure selectively to the resin composition of the invention, there may be adopted a method of projecting two or more bundles of ray of which wavelengths are twice as long as the wavelength suitable for cure and of which phases are identical with each other so that the bundles cross each other in the resin composition, thereby obtaining an energy beam necessary for cure by two photon absorption, and shifting the crossing position of bundles. Such bundles of ray identical in phase can be obtained from laser beam, for example.

Since the curing reaction of the composition of the invention is made to progress by cationic polymerization and radical polymerization caused by active energy beam, a crosslinking curing reaction of the composition can be effectively advanced by heating it at about 30-100°C at the time of irradiating the composition with energy beam, so far as the energy beam-curable cation-polymerizable organic substance (a) and energy beam-curable radical-polymerizable organic substance (c) allow such a crosslinking reaction.

Further. by subjecting the modelled product thus obtained to a heat treatment at 40-100°C or an ultraviolet irradiation treatment with UV lamp or the like, a modelled product of further improved mechanical properties can be obtained.

The resin composition for optical modelling of the present invention is a very excellent composition for forming a three-dimensional steric model by lamination of laminar products. A model can be prepared without die, and all types of shapes such as curved free surface and the like can be prepared by CAD/CAM and docking, so that industrial value of the composition is very high. The resin composition of the invention can be used in wide variety of fields including a model for examining appearance design in the midway of designing, a model for checking the matching of assemblage of parts, a wooden pattern for producing molding die, a follow-up controlling model for producing a metallic die, etc.

Concrete fields to which the resin composition of the invention can be applied include models of curved surfaces in automobile, electronic and electric parts, furniture, buildings, toys, containers, cast products, dolls, etc. and materials used for fabrication thereof.

[Working Examples]

Next, typical examples of the present invention are mentioned below. The present invention is by no means limited by these examples. In the examples, parts are by weight.

Example 1

As energy beam-curable cation-polymerizable organic substance (a), 65 parts of 3,4-epoxycyclohexylmethyl 3,4-epoxycyclohexanecarboxylate and 20 parts of 1,4-butanediol diglycidyl ether were used. As energy beam-sensitive cationic polymerization initiator (b), 3 parts of bis-[4-(diphenylsulfonio)-phenyl] sulfide bis-dihexafluoroantimonate was used. As an energy beam-curable radical-polymerizable organic substance (c), 15 parts of dipentaerythritol hexaacrylate was used. As an energy beam-sensitive radical polymerization initiator (d), 1 part of benzophenone was used. As a hydroxyl group-containing polyester (e), 15 parts of trimethylolpropane ϵ-caprolactone ester was used. The above-mentioned materials were thoroughly mixed together to prepare a resin composition for optical modelling. Using an experimental optical modelling system constituted of a three-dimensional NC (numerically controlled) table carrying a container for resin composition and a controlling part of which main parts are a helium-cadmium laser (wavelength 325 nm), an optical system and a personal computer, the resin composition was formed into a circular cone having a bottom diameter of 12 mm, a height of 15 mm and a thickness of 0.5 mm. The model thus formed was free from strain, very high in the accuracy of modelling, and excellent in mechanical properties.

For comparing the velocity of laser-induced polymerization, the period of time required for modelling was measured. The result was as short as 35 minutes. Further, for determining the accuracy of modelling, the bottom diameter of the conical modelled product was measured at arbitrarily selected 10 positions, and deviation was calculated. As a result, the mean deviation from the mean value (hereinafter referred to as accuracy of modelling) was 1.3%, demonstrating a high accuracy.

Example 2

As energy beam-curable cation-polymerizable organic substances (a), 50 parts of 3,4-epoxycyclohexylmethyl 3,4-epoxycyclohexanecarboxylate and 20 parts of 1,4-butanediol diglycidyl ether were used. As an energy beam-sensitive cationic polymerization initiator (b), 3 parts of triphenylsulfonium hexafluoroantimonate was used. As energy beam-curable radical-polymerizable organic substances (c), 20 parts of dipentaerythritol hexaacrylate and 10 parts of trimethylolpropane triacrylate were used. As an energy beam-sensitive radical polymerization initiator (d), 1 part of benzyl dimethyl ketal was used. As a hydroxyl group-containing polyester, 10 parts of glycerin ε-caprolactone ester was used. These ingredients were thoroughly mixed together to prepare a resin composition for optical modelling. Using the same laser type experimental optical modelling system as in Example 1, a bell-form modelled product was prepared. The modelled product thus obtained was free from strain, very high in the accuracy of modelling, and excellent in mechanical strengths. The resin composition used in this example was low in viscosity, easy to handle, and excellent in laser-curability.

In order to determine the velocity of laser polymerization and the accuracy of modelling, a conical product similar to that of Example 1 was prepared. As a result, the period of time required for modelling was 35 minutes, and the accuracy of modelling was 1.2%.

Example 3

As energy beam-curable cation-polymerizable organic substances (a), 10 parts of Bisphenol A diglycidyl ether, 40 parts of 3,4-epoxycyclohexylmethyl 3,4-epoxycyclohexanecarboxylate and 10 parts of vinylcyclohexene oxide were used. As an energy beam-sensitive cationic polymerization initiator (b), 2 parts of triphenylsulfonium hexafluoroantimonate was used. As energy beam-curable radical-polymerizable organic substances (c), 15 parts of Bisphenol A epoxyarylate and 25 parts of pentaerythritol triacrylate were used. As an energy beam-sensitive radical polymerization initiator (d), 2 part of 2,2-diethoxyaceto-phenone was used. As a hydroxyl group-containing polyester, 10 parts of triethylene glycol ε-caprolactone ester was used. These ingredients were thoroughly mixed together to prepare a resin composition for optical modelling. Using the same laser type experimental optical modelling system as in Example 1, the composition was made into a cup-form modelled product while heating the composition at 60°C. As a result, a product free from strain and excellent in the accuracy of modelling was obtained.

In order to determine the velocity of polymerization and the accuracy of modelling, a conical modelled product similar to that of Example 1 was prepared. As a result, the velocity of reaction was high due to the heating at 60°C, and the period of time required for modelling was as short as 25 minutes. The accuracy of modelling was 1.6%.

Example 4

As energy beam-curable cation-polymerizable organic substances (a), 55 parts of 3,4-epoxycyclohexylmethyl 3,4-epoxycyclohexanecarboxylate, 10 parts of 1,4-butanediol diglycidyl ether and 10 parts of triethylene glycol divinyl ether were used. As an energy beam-sensitive cationic polymerization initiator (b), 2 parts of bis-[4-(diphenylsulfonio)-phenyl] sulfide bis-dihexafluoroantimonate was used. As an energy beam-curable radical-polymerizable organic substance (c), 20 parts of dipentaerythritol hexaacrylate was used. As an energy beam-sensitive radical polymerization initiator (d), 1 part of benzophenone was used. As a hydroxyl group-containing polyester, 30 parts of 1,4-butanediol adipate was used. These ingredients were thoroughly mixed together to prepare a resin composition for optical modelling. Using the same laser type experimental optical modelling system as in Example 1, the composition was made into a bell-form modelled product. As a result, a product free from strain and excellent in mechanical strength, accuracy of modelling and surface smoothness was obtained.

In order to determine the velocity of polymerization and the accuracy of modelling, the same conical modelled product as in Example 1 was prepared. As a result, the period of time required for modelling was 30 minutes, and the accuracy of modelling was as good as 0.5%.

Comparative Example 1

An energy beam-curable cation-polymerizable resin composition was prepared by thoroughly mixing together 60 parts of 3,4-epoxycyclohexylmethyl 3,4-epoxycyclohexanecarboxylate, 20 parts of Bisphenol A diglycidyl ether, 20 parts of 1,4-butanediol diglycidyl ether and 3 parts of triphenylsulfonium hexafluoroantimonate. From th composition thus obtained, a conical product similar to that of Example 1 was prepared by means of the same laser type experimental optical modelling system as in Example 1. The modelled product thus obtained was free from strain and excellent in mechanical strengths. However, since the composition of this example was low in resolution at the time of laser-cure, surface of the modelled product was rough and accuracy of modelling was not good. Further, a period of several seconds was necessary from the time of laser irradiation to completion of polymerization, and the period of time required for modelling was as long as 120 minutes. The accuracy of modelling was as bad as 6.8%.

Comparative Example 2

An energy beam-curable radical-polymerizable resin composition was prepared by thoroughly mixing together 70 parts of Bisphenol A epoxyacrylate, 30 parts of trimethylolpropane triacrylate and 3 parts of benzyl dimethyl ketal. From the resin composition thus obtained, a conical modelled product similar to that of Example 1 was prepared by means of the same laser type experimental optical modelling system as in Example 1. The period of time required for modelling was 45 minutes. However, the modelled product involved strains due to great volume shrinkage at the time of cure, and the accuracy of modelling was as bad as 10.0%.

Comparative Example 3

An energy beam-curable cation/radical-polymerizable resin composition was prepared by thoroughly mixing together 65 parts of 3,4-epoxycyclohexylmethyl 3,4-epoxycyclohexanecarboxylate, 20 parts of 1,4-butanediol diglycidyl ether, 3 parts of bis-[4-(diphenylsulfonio)-phenyl]-sulfide bisdihexafluoroantimonate, 15 parts of dipentaerythritol hexaacrylate and 1 part of benzophenone. From the resin composition thus obtained, a conical modelled product similar to that of Example 1 was prepared by means of the same laser type experimental optical modelling system as in Example 1. The modelled product thus obtained was free from strain, and excellent in mechanical strengths. The period of time required for modelling was 50 minutes and the accuracy of modelling was 3.0%, demonstrating that this composition was on a considerable level as a resin composition for optical modelling. However, this composition was evidently inferior in properties to the compositions containing a hydroxyl group-containing polyester.

[Effect of the Invention]

Since the resin composition for use in optical modelling of the present invention is a mixed composition of an energy beam-curable cation-polymerizable organic substance and an energy beam-curable radical-polymerizable organic substance, the resin composition of the invention exhibit both the good characteristic properties of energy beam-curable cation-polymerizable organic substance and the good properties of energy beam-curable radical-polymerizable organic substance. A cation-polymerizable resin composition is not affected at all by the atmospheric oxygen at the time of curing reaction caused by active energy beam, and its volume shrinkage at the time of cure is small. Accordingly, a cation-polymerizable resin composition has a merit that its cured product is much prevented from crack formation and strain and excellent in strengths and, since such a composition can easily be endowed with a low viscosity, the period of time necessary for modelling can be shortened. However, such a composition has a fault that, since the polymerization reaction readily propagates from the energy beam-irradiated part to the neighboring areas at the time of active energy beam-caused curing reaction, the composition is low in resolution and a period of several seconds is necessary from the active energy beam-irradiation to the completion of polymerization. On the other hand, a radical-polymerizable resin composition has a merit that the polymerization reaction does not readily propagate from the irradiated part to the neighboring areas at the time of active energy beam-caused curing reaction and therefore such a composition is high in resolution, and such a composition requires no significant period of time from active energy beam-irradiation to completion of polymerization. However, such a composition has a fault that its polymerization is retarded by the atmospheric oxygen, it shows a great volume shrinkage at the time of cure, the cured product is inferior in mechanical strengths, and a low-viscosity composition of this type much irritates the skin and has an intense odor.

According to the present invention, (a) an energy beam-curable cation-polymerizable organic substance, (b) an energy beam-sensitive cationic polymerization initiator, (c) an energy beam-curable radical-polymerizable organic substance, (d) an energy beam-sensitive radical polymerization initiator and (e) a hydroxyl group-containing polyester are mixed together, and thereby a resin composition for use in optical modelling having the following characteristic features can be obtained. Thus, the resin composition of the present invention is hardly affected by the atmospheric oxygen: since the volume shrinkage at the time of cure can be made small, strains and cracks do not readily appear in the cured product; since a low-viscosity resin composition is readily obtained therefrom, the period of time required for modelling can be shortened; since the polymerization at the time of cure does not readily propagate from the active energy beam-irradiated part to the neighboring areas, resolution is good; no significant period of time is necessary from irradiation with active energy beam to completion of polymerization; the cured product has excellent mechanical strength and hardness; and the cationic polymerization can be accelerated so that curability is good. Thus, according to the present invention, there can be obtained a resin composition for optical modelling exhibiting a high curing velocity and a low volume shrinkage at the time of cure, and having a high accuracy of modelling.